

Types of Molecular Spectra:-

The Molecular Spectra can be divided into three spectral ranges corresponding to the different types of transitions b/w molecular energy states.

i) Electronic Spectra:- These spectra are observed both in emission and absorption in the visible and ultraviolet regions. Each spectrum consists of quite a large no. of bands. Each individual band has a sharp edge, called band-head, where the intensity falls suddenly to zero, and from this edge the intensity falls off gradually to the other side of the band. In fact, a band is composed of a series of lines which draw farther apart as the distance from the band-head increases. The band is said to be degraded toward the side opposite to the band-head. The electronic spectra are observed for heteronuclear as well as for the homonuclear diatomic molecules.

(ii) vibrational-rotational spectra:-

These spectra are observed in absorption in the near infrared region ($1 \mu - 10^2 \mu$, $1 \mu = 10^{-6} \text{ cm} = 10^4 \text{ \AA}$). Each spectrum consists of an intense band called fundamental band which is accompanied by a few weak bands. These bands like electronic bands have a fine structure. They are observed only for the heteronuclear molecules. The homonuclear molecules like H_2 , N_2 , O_2 do not produce vibrational rotational bands.

(iii) pure-rotational spectra:- These spectra are observed in absorption in the far infrared ($10^3 \mu - 10^5 \mu$) or in the microwave ($10^2 \mu - 10^4 \mu$) region. Each spectrum is composed of a series of nearly equidistant lines. Like vibrational-rotational

• Spectral, the pure rotational spectra are observed only for the heteronuclear diatomic molecules.

• The origin of different molecular spectra can be traced out in the different energy states of the molecule.

• Types of Molecular energy states and associated spectra:-

• Molecular energy states arise from the rotation of a molecule as a whole and from the vibrations of its constituent nuclei relative to one another as well as from changes in its electronic configuration.

• Rotational states are separated by quite small energy-interval ($\sim 10^3$ eV) and the spectra arising from transitions between these states are in the far infrared or microwave region.

• Vib. states are separated by some what larger energy intervals ($\sim 10^1$ eV) and the vibrational spectra fall in the near infrared region.

• The electronic states have higher energy separation (~ 10 eV) and the corresponding spectra fall in the visible and ultraviolet region.

• According to the Born-Oppenheimer picture of a molecule the electrons move rapidly in the field of the massive nuclei, and the nuclei move under slowly under their mutual electrostatic repulsion and the electronic energy of attraction. When two atoms are brought nearer to form a stable molecule, the electronic energy decreases rapidly while the energy of repulsion increases. For a certain internuclear separation the total potential energy becomes a minimum. This is the equilibrium internuclear separation. The two nuclei vibrate about their

equilibrium positions along the z-axis and the molecule rotates about the centre of mass.

The sch. eqn for the nuclear motion of a diatomic molecule is

$$\left[\frac{\hbar^2}{8\pi^2 M_1} \nabla_1^2 + \frac{\hbar^2}{8\pi^2 M_2} \nabla_2^2 + V(r) \right] \psi = E \psi$$

where M_1 & M_2 are masses of the nuclei, $V(r)$ is the potential energy function.

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

again, $\frac{1}{M_1} \nabla_1^2 \psi + \frac{1}{M_2} \nabla_2^2 \psi + \frac{8\pi^2}{h^2} [E - V(r)] \psi = 0$

eliminating the free particle motion and retaining only the internal motions, the eqn in the polar coordinates is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} [E - V(r)] \psi = 0$$

where $\mu = \frac{M_1 M_2}{M_1 + M_2}$

The angular equation and a radial eqn may be written as

$$\psi(r, \theta, \phi) = Y(\theta, \phi) R(r)$$

The angular eqn gives two solutions.

$$\Phi_M(\phi) = \frac{1}{\sqrt{2\pi}} e^{iM\phi}, \quad M = 0, \pm 1, \pm 2, \dots$$

$$\Theta_{J,M}(\theta) = \sqrt{\frac{2J+1}{2} \frac{(J-|M|)!}{(J+|M|)!}} P_{JM}(\cos \theta)$$

where $J = 0, 1, 2, \dots$ and $M = -J, \dots, +J$

The quantum no. J and M are associated with the angular momentum of the molecule.

$J(J+1) \frac{\hbar^2}{4\pi^2}$ is the square of the total angular momentum and $M \frac{\hbar}{2\pi}$ is the



z-Component of the angular momentum. The radial eqn is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{8\pi^2\mu}{\hbar^2} \left[E - V(r) - \frac{J(J+1)\hbar^2}{8\pi^2\mu r^2} \right] R = 0$$

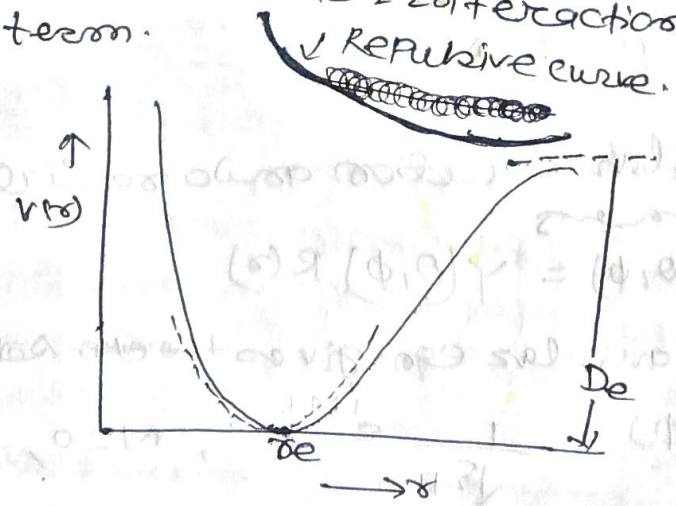
Substitute $R(r) = \frac{1}{r} S(r)$, we get

$$\frac{d^2S}{dr^2} + \frac{8\pi^2\mu}{\hbar^2} \left[E - V(r) - \frac{J(J+1)\hbar^2}{8\pi^2\mu r^2} \right] S = 0$$

This is the same as the eqn of a particle of mass μ moving along a line under a potential energy function $V(r) + \frac{J(J+1)\hbar^2}{8\pi^2\mu r^2}$.

The second term is the centrifugal potential energy term indicating a rotational motion superimposed on the linear vibrational motion of the particle.

Now $V(r) = E_e' + V_{nm}$ where E_e' is the eigenvalue of the electronic wave equation and V_{nm} is the nuclear-nuclear interaction (repulsion) energy term.



$$V(r) = V(r_e) + (r-r_e) \left(\frac{\partial V(r)}{\partial r} \right)_{r=r_e} + \frac{(r-r_e)^2}{2!} \left(\frac{\partial^2 V(r)}{\partial r^2} \right)_{r=r_e} + \frac{(r-r_e)^3}{3!} \left(\frac{\partial^3 V(r)}{\partial r^3} \right)_{r=r_e} + \dots$$

The 1st term $V(r_e)$ is a constant and can be set zero if we measure the potential energy

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relative to the minimum of the curve. The second term is zero because at $r=r_e$, $V(r)$ is a minimum so that its first derivative is zero. Thus

$$V(r) = \frac{(r-r_e)^2}{2!} \left(\frac{\partial^2 V(r)}{\partial r^2} \right)_{r=r_e} + \frac{(r-r_e)^3}{3!} \left(\frac{\partial^3 V(r)}{\partial r^3} \right)_{r=r_e} + \dots$$

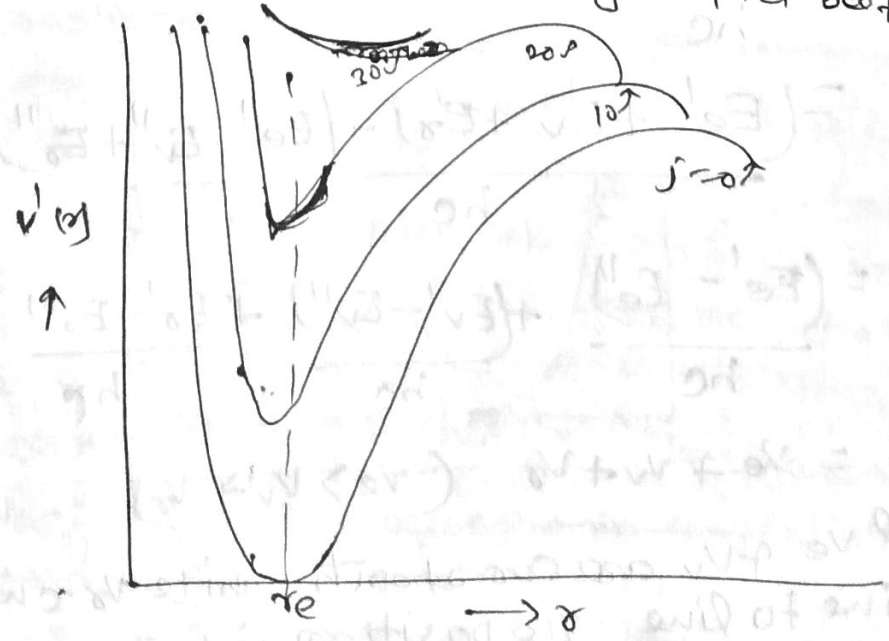
$V(r) = \frac{1}{2} k (r-r_e)^2$ where $k = \frac{\partial^2 V(r)}{\partial r^2}$ which represents a parabola

Thus the curve is parabolic near the minimum, and for small displacements $(r-r_e)$ the molecule may be treated as harmonic oscillator.

$$V'(r) = V(r) + \frac{j(j+1) \hbar^2}{8\pi^2 \mu r^2}$$

The rotation adds a term containing $\frac{1}{r^2}$ so that the effective potential curve shows a maximum between the minimum and the dissociation limit. Further j (rotation) increases, the minimum moves towards as well as outwards (or increases) and finally ceases to exist.

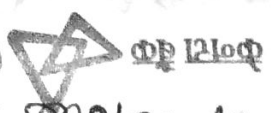
This is the molecule stretches as it rotates and becomes unstable for very rapid rotations.



$$E = E_e + E_{rot} + E_{vib}$$

E_e is the energy which the nuclei would possess if they were fixed.

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- The and contains of the K.E and P.E energies
- extra nuclear electrons and the potential energies of extra nuclear electron and the potential energy of separation of the nuclei.
- ~~Were fixed and consists of~~

- E_v is the vibrational energy which the molecule would possess if the nuclei executed vibrations and is defined by a single quantum number v .
- E_r is the additional rotational energy which the vibrating molecule would have if it rotated also.

If terms of wave no n

$$\frac{E}{hc} = \frac{E_e}{hc} + \frac{E_v}{hc} + \frac{E_r}{hc}$$

$$\text{or, } T = T_e + G(v) + F(v, J)$$

T_e is the electronic term.

$G(v)$ is the vibrational term and $F(v, J)$ is the rotational term.

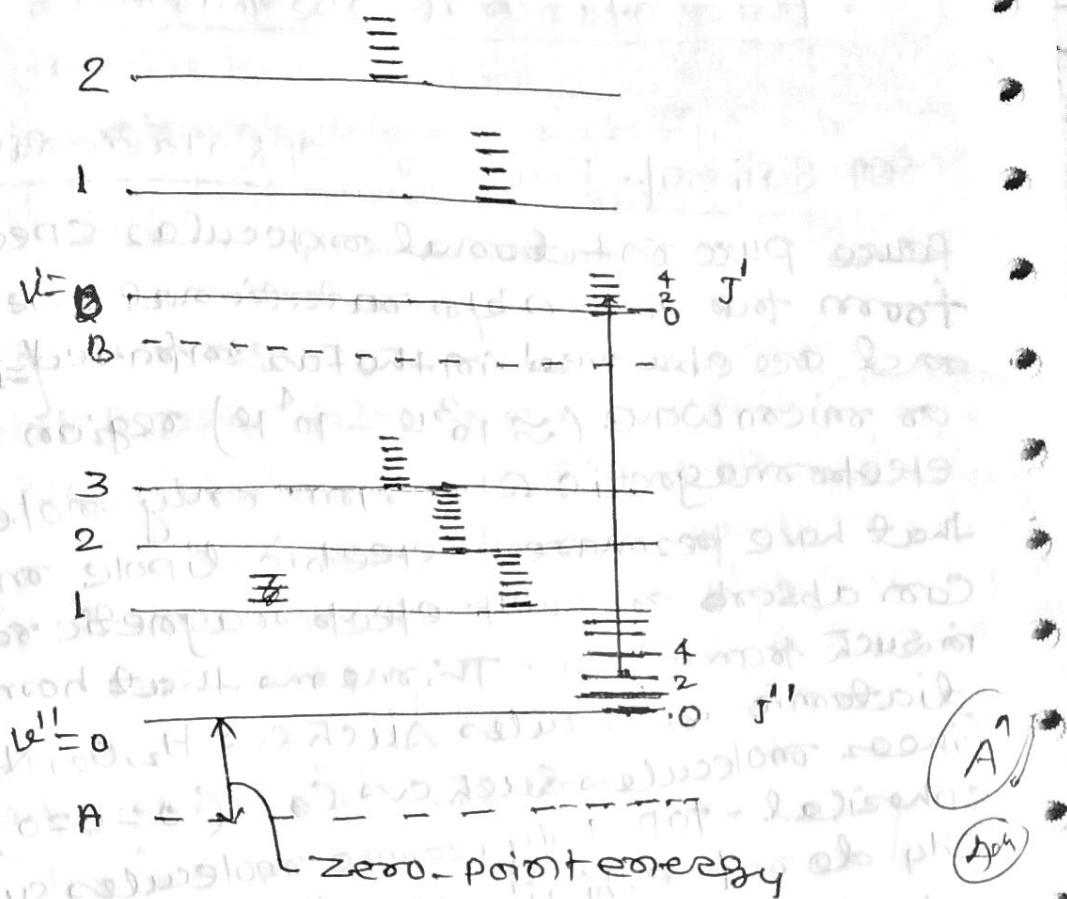
$$v = \frac{E' - E''}{hc}$$

$$= \frac{(E_e' + E_v' + E_r') - (E_e'' + E_v'' + E_r'')}{hc}$$

$$= \frac{(E_e' - E_e'')}{hc} + \frac{(E_v' - E_v'')}{hc} + \frac{(E_r' - E_r'')}{hc}$$

$$= v_e + v_v + v_r \quad (v_e > v_v > v_r)$$

band v_e & v_v are constants while v_r changes from line to line. The position in the band where $v_r = 0$ is called band origin. Its wave no. is $v_e + v_v$.



Besides electronic bands, we have non-electronic bands also for which $v_e = 0$. Such bands are of two types: -

(i) vibrational-rotational bands: - A vibrational

rotational band arises due to transition b/w two vibrational levels associated with the same electronic level. The lines of the band result from the transitions b/w the rotational levels of one vibrational level and the rotational levels of the other, so that the wave no. of a line is $\nu + \nu_r$. Such bands occur in the near infrared.

(ii) Pure rotational bands: -> These are other

lines, each of which arises from transition b/w rotational levels associated with one and the same vibrational level of a given electronic state. They occur in the far infrared or in the microwave region.